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(54) BASE MATERIAL FOR A HONEYCOMB FILTER AND MANUFACTURING METHOD THEREOF

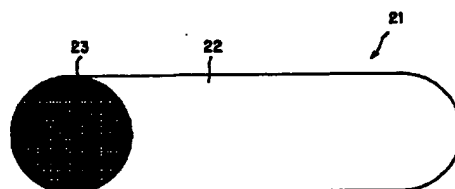
(57) ABSTRACT

PURPOSE

The purpose of this invention is to provide a type of base material for a honeycomb filter, characterized by the fact that it has a high mechanical strength and a high liquid permeability.

CONSTITUTION

Base material (22) for a honeycomb filter is made of a porous body with a honeycomb structure having multiple cells (23). The 50% particle size (D_{50}) of the aggregate particles that forms base material (22) is 40-100 μm ; 20-80 wt% of the aggregate particles are spherical particles with an aspect ratio of 1.1 or smaller, while the remaining portion is composed of non-spherical particles with an aspect ratio of 1.2 times or larger that of the spherical particles.



CLAIMS

1. A type of base material for a honeycomb filter, characterized by the following facts:
the base material for a honeycomb filter is made of a porous body with a honeycomb structure having multiple cells;

The 50% particle size (D_{50}) of the aggregate particles that form the base material is 40-100 μm ; 20-80 wt% of the aggregate particles are spherical particles with an aspect ratio of 1.1 or smaller, while the remaining portion is composed of non-spherical particles with an aspect ratio of 1.2 times or larger that of the spherical particles.

2. The base material for a honeycomb filter described in Claim 1, characterized by the fact that the particle size distribution of the aggregate particles satisfies the following relationships (1) and (2):

$$0.7 \times D_{50} \leq D_{20} \quad (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad (2)$$

(where D_{20} : 20% particle size, D_{50} : 50% particle size, D_{80} : 80% particle size)

3. A type of base material for a honeycomb filter characterized by the following facts:
the base material for a honeycomb filter is made of a porous body having a honeycomb structure with multiple cells;

The 50% pore size (d_{50}) is 5-25 μm ; and the pore size distribution measured using the mercury press-in method satisfies following relationships (3) and (4).

$$0.75 \times d_{50} \leq d_{20} \quad (3)$$

$$d_{80} \leq 1.25 \times d_{50} \quad (4)$$

(where d_{20} : 20% pore size, d_{50} : 50% pore size, and d_{80} : 80% pore size).

4. A method for manufacturing base material for a honeycomb filter, characterized by the following facts:

in this method for manufacturing base material for a honeycomb filter, there is a step in which a composition containing aggregate particles is extruded from nozzle having a shape complementary to that of the honeycomb structure for molding;

in this operation, the composition is prepared from aggregate particles with the following feature: the proportion of spherical particles with a 50% particle size (D_{50}) of 40-100 μm and with an aspect ratio of 1.1 or smaller is 20-80 wt%, and the remaining portion is composed of non-spherical particles with an aspect ratio 1.2 times or larger that of said spherical particles.

5. The method for manufacturing base material for a honeycomb filter described in Claim 4, characterized by the fact that the spherical particles are prepared by the spray drying method.

6. The method for manufacturing base material for a honeycomb filter described in Claim 4 or 5, characterized by the fact that the particle size distribution of the aggregate particles for preparing the composition satisfies the following relationships (1) and (2):

$$0.7 \times D_{50} \leq D_{20} \quad (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad (2)$$

(where D_{20} : 20% particle size, D_{50} : 50% particle size, D_{80} : 80% particle size).

7. The base material for a honeycomb filter described in any of Claims 1-3, characterized by the fact that on the inner peripheral surface of the cells of the base material for a honeycomb filter, there is at least one layer of filtering film having a 50% pore size smaller than that of the inner peripheral surface of the cells.

DETAILED EXPLANATION OF THE INVENTION

[0001]

TECHNICAL FIELD OF THE INVENTION

This invention pertains to a type of base material for a honeycomb filter made of a porous body with a honeycomb structure having multiple cells. More specifically, this invention pertains to a type of base material for a honeycomb filter characterized by the fact that it has a high mechanical strength and a high fluid permeability.

[0002]

PRIOR ART

For a honeycomb filter, such as the filter having base material (22) made of a porous body with a honeycomb structure having multiple cells (23) shown in Figure 1, gas, liquid or other fluid for processing fed to multiple cells (23) permeates through the pores of the porous body for filtering. Consequently, the filtering area per unit volume is large. These filters are thus widely used as dust collecting filters, solid-liquid separating filters, etc.

[0003]

For example, filter (21) has a structure in which the filter is accommodated in a housing, and the outer peripheral surface side and end surface side of base material (22) are gas-tightly isolated by means of O-rings, etc. In this structure, in the fluid under processing and fed to cells (23), only the filtered fluid that passes through pores of the base material can flow out from the outer peripheral surface side, and the fluid under processing that is not filtered is recovered from the end surface side in this cross-flow filter.

[0004]

For the honeycomb filter, the structure has at least one layer of filtering film with a pore size (0.01-1.0 μm) that is even smaller than that of the pore size of the pores of the base material on the inner peripheral surface of cells (23), with it being ideal that the structure have a pore size of the inner portion of the base material that is as large as possible. In this structure, due to the filtering film with a small pore size, the filtering performance is ensured. On the other hand, when the pore size is large (about 1 to more than 100 μm), the base material has a low flow resistance with respect to the interior. Consequently, the fluid permeability can be expected to increase.

[0005]

Usually, the base material for a honeycomb filter is manufactured using a molding method in which a composition containing aggregate particles is extruded from nozzle having a shape complementary to that of the honeycomb structure. In the prior art, there are several methods for forming a base material with a large pore size, such as [1] a method in which the particle size of aggregate particles is increased to have larger pores as gaps among aggregate particles (hereinafter referred to as "first method") and [2] a method in which the organic substances (pitch, coke, etc.) that are burned off during sintering of the base material are added to the composition so as to form gaps and to have pores larger than those formed in the other methods (hereinafter referred to as "second method").

[0006]

PROBLEMS TO BE SOLVED BY THE INVENTION

However, for said first method, the obtained base material fails to have a sufficient mechanical strength for use as a filter. More specifically, in the film forming step of the operation for manufacturing the filter film on the inner peripheral surface of cells of the base material, damage due to handling leads to a lower yield of products or, when the filter is in use, damage may occur under the pressure of a back-flow cleaning operation, which is undesired.

[0007]

On the other hand, for said second method, it is hard to increase the pore size and to increase the water permeability. In addition, when the base material is sintered, the organic substances are rapidly burned off. Consequently, cracks occur under thermal impact.

[0008]

Consequently, in the prior art, there is yet no base material for a honeycomb filter with a high mechanical strength and a high fluid permeability. There is a high demand on the development of such a base material for a honeycomb filter. The purpose of this invention is to solve the aforementioned problems of the conventional methods by providing a type of base material for a honeycomb filter with a high mechanical strength and high liquid permeability.

[0009]

MEANS TO SOLVE THE PROBLEMS

In order to solve the aforementioned problems, the present inventors have performed extensive research. As a result of this research work, it was found that by controlling the 50% particle size of the aggregate particles to form the base material and the mass proportion of the

spherical particles within prescribed ranges, respectively, the problems of the prior art can be solved. As a result, this invention was reached.

[0010]

That is, this invention provides a type of base material for a honeycomb filter characterized by the following facts: the base material for a honeycomb filter is made of a porous body with a honeycomb structure having multiple cells; the 50% particle size (D_{50}) of the aggregate particles that form the base material is 40-100 μm ; 20-80 wt% of the aggregate particles are spherical particles with an aspect ratio of 1.1 or smaller, while the remaining portion is composed of non-spherical particles with an aspect ratio of 1.2 times or larger than that of the spherical particles.

[0011]

The particle size distribution of the aggregate particles preferably satisfies the following relationships (1) and (2).

$$0.7 \times D_{50} \leq D_{20} \quad (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad (2)$$

(where D_{20} : 20% particle size, D_{50} : 50% particle size, D_{80} : 80% particle size).

[0012]

Also, this invention provides a type of base material for a honeycomb filter characterized by the following facts: the base material for a honeycomb filter is made of a porous body having a honeycomb structure with multiple cells; the 50% pore size (d_{50}) is 5-25 μm ; and the pore size distribution measured using the mercury press-in method satisfies following relationships (3) and (4).

$$0.75 \times d_{50} \leq d_{20} \quad (3)$$

$$d_{80} \leq 1.25 \times d_{50} \quad (4)$$

(where d_{20} : 20% pore size, d_{50} : 50% pore size, and d_{80} : 80% pore size).

[0013]

In addition, this invention provides a method for manufacturing base material for a honeycomb filter characterized by the following facts: in this method for manufacturing base material for a honeycomb filter, there is a step in which a composition containing aggregate particles is extruded from nozzle having a shape complementary to that of the honeycomb structure for molding; in this operation, the composition is prepared from aggregate particles with the following feature: the proportion of spherical particles with a 50% particle size (D_{50}) of

40-100 μm and with an aspect ratio of 1.1 or smaller is 20-80 wt%, and the remaining portion is composed of non-spherical particles with an aspect ratio 1.2 times or larger than that of said spherical particles.

[0014]

For the method used to manufacture base material for a honeycomb filter in this invention, the spherical particles are preferably prepared by the spray drying method, and the particle size distribution of the aggregate particles for preparing the composition preferably satisfies the following relationships (1) and (2):

$$0.7 \times D_{50} \leq D_{20} \quad (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad (2)$$

(where D_{20} : 20% particle size, D_{50} : 50% particle size, D_{80} : 80% particle size).

[0015]

In addition, this invention provides a type of base material for a honeycomb filter characterized by the fact that on the inner peripheral surface of the cells of the base material for a honeycomb filter, there is at least one layer of filtering film having a 50% pore size smaller than that of the inner peripheral surface of the cells.

[0016]

EMBODIMENT OF THE INVENTION

For the base material used for a honeycomb filter of this invention, the 50% particle size of the aggregate particles that form the base material and the weight proportion of the spherical particles are controlled within prescribed ranges, respectively. For the base material for a honeycomb filter in this invention, the mechanical strength is high and the fluid permeability is high. In the following, this invention will be explained in more detail.

[0017]

(1) BASE MATERIAL

For the base material for a honeycomb filter (hereinafter referred to as "base material") in this invention, among the aggregate particles, at least one type of aggregate particles are spherical particles having an aspect ratio of 1.1 or smaller. Using such spherical particles as aggregate particles, even after sintering of the base material, gaps (that is, pores) are reliably formed among the aggregate particles, and the fluid permeability can be increased. More specifically, by having a proportion of said spherical particles in the aggregate particles of 20%

or higher, the fluid permeability is increased, and the fine structure inside the base material becomes more uniform.

[0018]

However, if all of the aggregate particles that form the base material are said spherical particles, bonding between the aggregate particles becomes weaker, and the mechanical strength of the base material decreases. Consequently, in addition to the aforementioned requirement that the proportion of the spherical particles among aggregate particles be 20 wt% or more, there should be an upper limit set at 80 wt%.

[0019]

Among the aggregate particles, the remaining portion in addition to the spherical particles is made of non-spherical particles with an aspect ratio 1.2 times or more than that of said spherical particles. That is, when spherical particles having an aspect ratio of 1.0 are used, the non-spherical particles should have an aspect ratio of 1.2 or larger. When spherical particles having an aspect ratio of 1.1 are used, the non-spherical particles should have an aspect ratio of 1.32 or larger. Although the non-spherical particles are undesired from the viewpoint of the increase in the fluid permeability, they nevertheless have the effect of strengthening bonds between the aggregate particles, so that they act to increase the mechanical strength of the base material.

[0020]

In this invention, "aspect ratio" is defined as the average value of the aspect ratio (ratio of longer edge to shorter edge) of 20 aggregate particles randomly selected from a microgram taken for a powder sample on a scanning electron microscope, or the average value of the aspect ratio calculated in the same way for the plane prepared by coating a resin (such as an epoxy resin) on the cut plane of a sintered body to bury holes, followed by finishing to a mirror-surface quality.

[0021]

For the spherical particles and non-spherical particles, in addition to the aforementioned requirement on the aspect ratio, it is also necessary for the 50% particle size (D_{50}) to be in a prescribed range, or specifically in the range of 40-100 μm . If the 50% particle size (D_{50}) is smaller than 40 μm , the fluid permeability decreases. On the other hand, if it is larger than 100 μm , the mechanical strength of the base material decreases. This is undesirable as well. Also, by having a 50% particle size (D_{50}) of 40-100 μm , it is possible to control the 50% pore size (d_{50}) of the base material in the range of 5-25 μm (measured using the mercury press-in method).

[0022]

Also, according to this invention, “x% particle size” refers to the particle size measured using the sieve separating method in the powder state. More specifically, multiple sieves with different nominal opening sizes are stacked, with sieves having a larger opening set higher. A powder sample as the object for measurement of the particle size is poured on the uppermost sieve. After shaking with a machine for 15 min, from the relationship between the mass of powder on each sieve and the opening size of the sieve, a particle size distribution curve is drawn, and the particle size with an integrated mass of x% is defined as the x% particle size.

[0023]

For the spherical particles and non-spherical particles, in addition to the aforementioned requirement on the proportion of spherical particles and 50% particle size (D_{50}), it is necessary that the particle size distribution be controlled to within a prescribed range. More specifically, it is preferred that following relationships (1) and (2) be met.

$$0.7 \times D_{50} \leq D_{20} \quad (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad (2)$$

(where D_{20} : 20% particle size, D_{50} : 50% particle size, D_{80} : 80% particle size)

[0024]

When said relationships (1) and (2) are satisfied for the particle size distribution of the aggregate particles, the base material's pore size distribution is sharp. More specifically, the pore size distribution measured using the mercury press-in method is controlled to within the range defined by following relationships (3) and (4) for the base material.

$$0.75 \times d_{50} \leq d_{20} \quad (3)$$

$$d_{80} \leq 1.25 \times d_{50} \quad (4)$$

(where d_{20} : 20% pore size, d_{50} : 50% pore size, d_{80} : 80% pore size).

[0025]

On the other hand, when said relationship (1) is not satisfied, the amount of the fine particles becomes larger, so that gaps among the aggregate particles of the base material are clogged, and the fluid permeability tends to decrease. Also, when said relationship (2) is not satisfied, the gap between aggregate particles becomes larger. However, in the film manufacturing process, the slurry for forming the film enters the gap to clog it. Consequently, the fluid permeability of the filter may still decrease.

[0026]

According to this invention, “x% pore size” refers to the pore size measured using the mercury press-in method with its principle based on following relationship (5). More specifically, for a dry base material, while the pressure is slowly increased, mercury is pressed in. As mercury is sequentially pressed into pores with a larger size, then into pores with a smaller size, the accumulation volume of mercury increases. Finally, all of the pores are filled with mercury, and the accumulation volume reaches equilibrium. According to this invention, pore size d calculated from pressure P when the accumulation volume becomes x% is defined as x% pore size.

$$d = -\gamma \times \cos\theta / P \quad (5)$$

(where d : pore size, γ : surface tension, θ : contact angle, P : pressure)

[0027]

(2) MANUFACTURING METHOD

The base material for a honeycomb filter is prepared by extruding a composition containing aggregate particles from a nozzle having a shape complementary to that of the honeycomb structure for molding, followed by drying and sintering of the molding. When the base material of this invention is manufactured, as the composition is prepared, aggregate particles with the aspect ratio, 50% particle size, and particle size distribution within said ranges are used.

[0028]

That is, a composition is prepared from aggregate particles, which have the following features: 50% particle size (D_{50}) of 40-100 μm , 20-80 wt% of the aggregate particles are spherical particles with an aspect ratio of 1.1 or smaller, while the remaining portion is composed of non-spherical particles with an aspect ratio of 1.2 times or larger that of the spherical particles. When the pore size distribution of the base material has to be sharp, the particle size distribution of the aggregate particles should satisfy the following relationships (1) and (2).

$$0.7 \times D_{50} \leq D_{20} \quad (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad (2)$$

(where D_{20} : 20% particle size, D_{50} : 50% particle size, D_{80} : 80% particle size).

[0029]

An example of the method for preparing it is as follows: Commercially available ceramic feed materials are used as aggregate particles either directly or after crushing and classification;

two or more types of aggregate particles are mixed appropriately to meet the aforementioned conditions.

[0030]

In the manufacturing method in this invention, it is preferred that the spherical particles be prepared using the spray drying method. Also, spherical particles may be prepared by crushing and mixing using a crusher and a blender (ball mill, etc.). On the other hand, using the spray drying method, in which a liquid feed material is granulated and dried using a spray drier, followed by sintering, it is relatively easy to obtain spherical particles with an aspect ratio of 1.1 or smaller. Also, because the particles prepared using the spray drying method have a smoother surface than that of the particles prepared by crushing, they do not harm the extrusion molding nozzle, so that the lifetime of the nozzle can be prolonged by about 10 times.

[0031]

The manufacturing method in this invention may be the same as the conventional manufacturing method, except that when the composition is prepared, the 50% particle size and the particle size distribution of the aggregate particles should be controlled to within prescribed ranges.

[0032]

In addition to aggregate particles, the composition also contains a dispersing medium, organic binder, and, as needed, an inorganic binder, surfactant, plasticizer, etc. These components are mixed and blended to form a feed material for molding.

[0033]

Examples of aggregate particles include alumina, mullite, Scherben [transliteration], cordierite, and silicon carbide, as well as their mixtures. Examples of dispersing agents include water, etc. Examples of organic binders include methylcellulose, etc.

[0034]

The inorganic binder is an additive for strengthening bonds among aggregate particles. Examples include the following particles with a particle size of 1 μm or smaller: alumina, silica, zirconia, titania, glass frit, feldspar, and cordierite, which may be used either alone or as a mixture of several types. Also, although an inorganic binder is a type of ceramic particle, it is not included in the aggregate particles in this invention.

[0035]

The amount of the inorganic binder added with respect to 100 wt% of the weight of the aggregate particles is preferably in the range of 15-35 wt%. If the amount is less than 15 wt%, the strength of the base material decreases. On the other hand, if the amount is over 35 wt%, although a sufficient strength is realized, the gaps among the aggregate particles are nevertheless filled with the inorganic binder, so that pores in the base material are clogged, leading to a decrease in the fluid permeability.

[0036]

The composition is extrusion molded to a prescribed shape, followed by drying and sintering to manufacture a base material of the honeycomb structure. For example, the composition may be loaded in a mono axial, biaxial, or multi axial screw extruder or plunger extruder, or some other conventional extruder, and it is extruded from a nozzle having a shape complementary to that of the honeycomb structure of the base material used to form a molding.

[0037]

Depending on the shape of the nozzle, it is possible to select the desired shape for the end surface (circular, square, rectangular, hexagonal, etc.), outer diameter of the end surface (30-200 mm \varnothing for the circular shape), diameter of the inscribed circle (usually in the range of 2-5 mm \varnothing), etc., of the base material. There is no special limitation on the size of the base material. Usually, the total length in the longitudinal direction is about 150-2000 mm.

[0038]

(3) FILTER

After attaching a slurry containing aggregate particles for forming a film on the inner peripheral surface of the cells of said base material, the film-formed body is dried and sintered to form a filtering film. In this way, a honeycomb filter can be obtained.

[0039]

For example, using a conventional method, such as the dipping film forming method, or the filtering film forming method described in Japanese Kokoku Patent Application No. Sho 63[1988]-66566 that has been disclosed by the present patent applicant, a film forming slurry prepared by dispersing aggregate particles in water or some other dispersing medium, with an organic binder, pH adjusting agent, surfactant, etc., added as needed, is applied to form a film on the inner peripheral surface of cells, followed by drying and high-temperature sintering at about 1300°C for the film-formed body to form a filter. The types of aggregate particles, dispersing

medium, and organic binder used in this case may be the same as those for preparing the base material. However, in order to reduce the pore size of the filtering film, usually, the 50% particle size of the aggregate particles is smaller than that of the base material.

[0040]

Also, with the same purpose as that for the base material, the film forming slurry may also contain an inorganic binder. For the filtering film, the ingredient binders that may be used include the following types of particles with a particle size of 1 μm or smaller: clay, kaolin, titania sol, silica sol, glass frit, etc. The total weight of the aggregate particles and inorganic binder among the total weight is preferably 5-25 wt%.

[0041]

Also, it is necessary to form at least one layer of the filtering film. However, it is also possible to form two or more laminated layers.

[0042]

APPLICATION EXAMPLES

In the following, this invention will be explained in detail with reference to application examples. However, this invention is not limited to these application examples.

[0043]

As ceramic feed material for the aggregate particles of the base material, alumina (A1-A6), mullite (M1-M3), and Scherben (S1), with compositions and aspect ratios listed in Table 1 were used. These feed materials were mixed in proportions listed in Tables 2-3 to form aggregate particles.

[0044]

Also, for A3 and M1, after the feed material was prepared in liquid form, a spray dryer was used for granulation and drying, followed by sintering to form [particles] with an aspect ratio of 1.1 or smaller.

[0045]

[Table 1]

Symbol	Type	Particle size distribution					Aspect ratio	
		D50 x 0.7 μm	D20 μm	D50 μm	D80 μm	D50 x 1.3 μm	Average value	Particle with [aspect ratio] of 1.1 or smaller %
A1	Alumina	60	62	85	106	111	1.8	0
A2		49	55	70	86	91	1.9	0
A3		53	65	75	85	98	1.1	100
A4		74	92	105	135	137	1.8	0
A5		18	18	26	33	34	1.8	0
A6		53	41	75	105	98	1.7	0
M1	Mullite	53	65	76	85	99	1	100
M2		46	45	65	87	85	1.5	0
M3		55	62	78	104	101	1.8	0
S1	Scherben	49	54	70	87	91	1.8	0

[0046]

(BASE MATERIAL)

An inorganic binder (feldspar, glass frit, etc.), water, and methylcellulose as an organic binder were added to said aggregate particles, then the mixture was blended to form a composition for extrusion molding, forming a honeycomb-structure extruded molding with an outer diameter of 30 mm \varnothing , and having 37 cells with diameter of 2.4 mm \varnothing . The amount of the inorganic binder with respect to 100 wt% of the mass of the aggregate particles was 25 wt%. The extruded molding was sintered in an electric oven at 1500°C to form a base material.

[0047]

For said base material, an evaluation was made with respect to the 50% particle size, pore size distribution, and mechanical strength.

[0048]

The 50% particle size and pore size distribution of the base material were measured using the mercury press-in method as follows. First of all, a specimen with a length of 25 mm from the end surface was cut out. A piece with 4-5 cells left on it was then cut out to form a sample for measurement. The sample was dipped in mercury, then mercury was pressed in. The accumulation volume was measured and was used to calculate the 20% pore size, 50% pore size, and 80% pore size.

[0049]

The mechanical strength of the base material was evaluated as follows: A cylindrical extrusion molding prepared from the composition for molding and having dimensions of 20 mm \varnothing in diameter x 100 mm in length was dried and sintered in the same way as for the base material. With a distance between supporting points of 80 mm, the 3-point flexural strength of the sintered sample was measured for evaluation.

[0050]

For the filter prepared by forming a filtering film on said base material, the performance was also evaluated. The filtering film had a laminated structure, including an intermediate layer and filtering layer.

[0051]

The intermediate layer and filtering layer were prepared using the filtering film forming method described in Japanese Kokai Patent Application No. Sho 61[1986]-238315. More specifically, as shown in Figure 2, on equipment having vacuum chamber (6), storage container (8), pump (7), flanges (2), (3), pipeline (10), etc., the cell inner peripheral surface side of base material (1), which had the interior of cells substituted with water or some other liquid, and the outer peripheral surface side of base material (1) were fixed in a gas-tight separated state with flanges (2), (3), and bolts (5). Slurry (9) in storage container (8) was then fed continuously into the cells of base material (1) by means of pump (7) to make contact with cell inner peripheral surface (12), while vacuum chamber (6) was evacuated by means of vacuum pump (13), so that the outer peripheral surface side of base material (1) was in a reduced pressure state. By means of this operation, a difference in pressure for filtering was applied between the outer peripheral surface side of base material (1) and the side of cell inner peripheral surface (12). Consequently, the slurry formed a film on cell inner peripheral surface (12) of base material (1), and the water content in the slurry was exhausted as a filtrate from the outer peripheral surface side of base material (1).

[0052]

(INTERMEDIATE LAYER)

A slurry was prepared from aggregate particles made of the same feed material as that for the base material having a 50% particle size (D_{50}) of 3.2 μm , inorganic binder (feldspar, glass frit, etc.), and water in a weight ratio of 27:3:70. After a film of slurry was formed on the inner peripheral surface of the cells, drying and sintering were performed to form an intermediate layer of film fixed on the base material.

[0053]

(FILTERING LAYER)

A slurry was prepared from aggregate particles made of the same feed material as that for the base material having a 50% particle size (D_{50}) of 0.4 μm , inorganic binder (glass frit), and water in a weight ratio of 9:1:90. After a film of slurry was formed on the surface of the intermediate layer, drying and sintering were performed to form a filtering layer fixed on the intermediate layer.

[0054]

For the filter manufactured in the above process, the fluid permeability was evaluated by means of the water permeating rate, and the filtering performance was evaluated by means of the maximum pore size of the filtering layer. The water permeation rate was evaluated as follows: After degassing of the cells inside the filter in water under a reduced pressure of 6.7 kPa or lower for 2 h, pure water was injected into the cells of the filter under a pressure difference of 4.8-9.8 kPa and at 25°C, then it was filtered from inside the cells to the filter's outer peripheral surface side. The amount of water permeated per unit filtering area per unit time was measured for evaluation.

[0055]

The maximum pore size of the filtering layer was measured using the following method. According to the air flow method described in ASTM F316, for a filter wetted with water at a water temperature of 20°C, the pressure was slowly raised, while pressurized air was fed from the cell's inner peripheral surface. From pressure P at which the first gas bubble emerges from the base material's outer peripheral surface, pore size D was calculated and taken as the maximum pore size of the filtering layer.

[0056]

APPLICATION EXAMPLE 1

In Application Example 1, base materials were prepared from aggregate particles made of alumina particles having various proportions of spherical particles, 50% particle sizes, and particle size distributions. A filtering film was then formed to obtain filters.

[0057]

[Table 2]

Table 2]	Aggregate particles										Base material					Filtering film		Filtering layer's maximum pore size
	Composition		Particle size distribution					Proportion of particles with aspect ratio of 1.1 or smaller in the feed material	Average pore size					Flexural strength	Water permeability	50% particle size of aggregate particles		
																Intermediate layer	Filtering layer	
	Type of aggregate 1	Type of aggregate 2	D50 x 0.7	D20	D50	D80	D50 x 1.3	%	d50 x 0.75	d20	d50	d80	d50 x 1.25	μm	μm	μm		
%	%	μm	μm	μm	μm	μm	%	μm	μm	μm	μm	μm	MPa	M ³ /hr·m ²	μm	μm		
Comparative Example 1-1	A1 0	A3 100	53	65	75	85	98	100	12.2	13.9	16.3	18.4	20.4	16.5	72.7	-	-	
Comparative Example 1-2	A1 20	A3 80	53	64	75	86	98	80	12.4	13.9	16.5	18.7	20.7	18.7	72.7	-	-	
Application Example 1-1	A1 25	A3 75	53	63	76	88	98	75	12.5	13.9	16.7	19.6	20.8	33.1	73.8	3.6	0.7	
Application Example 1-2	A1 50	A3 50	54	62	77	92	100	50	12.7	13.7	17.0	20.2	21.2	32.5	75.0	3.6	0.7	
Application Example 1-3	A1 75	A3 25	55	62	78	97	101	25	13.0	13.0	17.3	21.2	21.7	31.9	76.2	3.6	0.7	
Comparative Example 1-3	A1 80	A3 20	55	61	78	101	101	20	13.2	13.2	17.6	22.9	22.0	31.9	76.2	3.6	0.7	
Comparative Example 1-4	A2 20	A3 80	52	63	74	85	96	80	12.1	13.5	16.1	18.3	20.1	19.3	71.5	-	-	
Application Example 1-4	A2 25	A3 75	52	62	74	86	96	75	12.0	13.3	16.0	18.9	20.0	34.3	71.5	3.6	0.7	
Application Example 1-5	A2 50	A3 50	51	60	73	86	95	50	11.7	12.7	15.7	18.4	19.6	34.8	70.3	3.6	0.7	
Application Example 1-6	A2 75	A3 25	50	57	71	87	92	25	11.2	11.7	15.0	18.0	18.7	36.0	68.0	3.6	0.7	
Comparative Example 1-5	A2 80	A3 20	49	56	70	87	91	20	11.0	11.4	14.7	18.4	18.4	36.8	66.8	3.6	0.7	
Comparative Example 1-6	A4 20	A3 80	53	67	76	95	99	80	12.8	14.9	17.1	21.2	21.4	18.1	73.8	-	-	
Application Example 1-7	A4 25	A3 75	56	70	78	99	101	75	13.0	15.5	17.3	20.8	21.7	31.9	76.2	3.6	0.7	
Application Example 1-8	A4 50	A3 50	62	72	88	113	114	50	15.5	16.7	20.7	24.8	25.8	26.1	87.8	3.6	0.7	
Comparative Example 1-7	A4 75	A3 25	71	77	102	125	133	25	19.0	18.8	25.3	30.6	31.7	17.9	104.2	-	-	
Comparative Example 1-8	A4 80	A3 20	74	85	105	128	137	20	19.7	20.9	26.3	32.2	32.9	16.2	107.7	-	-	
Comparative Example 1-9	A5 20	A3 80	51	30	73	83	95	80	11.9	9.4	15.9	18.7	19.9	19.8	70.3	-	-	
Comparative Example 1-10	A5 25	A3 75	50	26	72	80	94	75	11.5	9.1	15.3	18.6	19.2	35.4	69.2	3.6	0.7	
Comparative Example 1-11	A5 50	A3 50	29	20	41	88	53	50	6.2	5.8	8.3	9.1	10.4	53.5	33.0	-	-	
Comparative Example 1-12	A5 75	A3 25	19	19	27	63	35	25	4.1	3.9	5.6	6.5	6.9	61.7	16.7	-	-	
Comparative Example 1-13	A5 80	A3 20	18	18	25	35	33	20	4.0	3.6	5.3	6.7	6.6	62.8	14.3	-	-	
Comparative Example 1-14	A6 20	A3 80	53	63	75	86	98	80	12.1	13.3	16.1	18.3	20.1	18.7	71.1	-	-	
Application Example 1-9	A6 25	A3 75	53	61	75	88	98	75	12.3	13.2	16.4	19.5	20.5	33.4	70.2	3.6	0.7	
Application Example 1-10	A6 50	A3 50	53	55	75	92	98	50	12.2	12.3	16.2	19.8	20.3	33.1	69.8	3.6	0.7	
Application Example 1-11	A6 75	A3 25	53	54	75	100	98	25	12.0	12.1	16.0	19.8	20.0	33.8	72.3	3.6	0.7	
Comparative Example 1-15	A6 80	A3 20	53	45	75	103	98	20	12.5	9.6	16.6	22.9	20.8	32.9	73.1	3.6	0.7	

[0058]

(RESULTS)

As listed in Table 2, in Application Examples 1-1 to 1-11, in which the proportion of the spherical particles among the aggregate particles and the 50% particle size are controlled to within the ranges defined in this invention, good results were obtained with respect to the base material's flexural strength, base material's water permeability, and the maximum pore size of the filtering layer.

[0059]

On the other hand, in Comparative Examples 1-1, 1-2, -14, 1-6, 1-9, and 1-14, in which the proportion of the spherical particles among the aggregate particles is over 80 wt%, and in Comparative Examples 1-7 and 1-8, in which the 50% particle size is over 100 μm , the base material's flexural strength is lower than 20 MPa. That is, the flexural strength is significantly lower than that in the application examples.

[0060]

Also, in Comparative Examples 1-12 and 1-13, in which the 50% particle size is smaller than 40 μm , the base material's water permeability is much lower (lower than 20 $\text{m}^3/\text{h} \cdot \text{m}^2$). In addition, in Comparative Examples 1-3, 1-5, and 1-15, in which the proportion of the spherical particles among the aggregate particles is less than 20 wt%, the maximum pore size of the filtering layer is too large. As a result, the fine structure inside the base material becomes non-uniform, and when the film is formed, slurry unevenly attaches on the base material.

[0061]

In Application Examples 1-1 to 1-11, in which the particle size distribution of the aggregate particles is within the range defined in this invention, for the pore size of the base material, d_{20} is 0.75 times d_{50} or larger, and d_{80} is 1.25 times d_{50} or smaller. That is, the pore size distribution is sharp. On the other hand, in Comparative Examples 1-10 and 1-11—in which, although the proportion of the spherical particles and 50% particle size meet the requirements, the particle size distribution is nevertheless outside the range of this invention—with respect to the pore size distribution of the base material, d_{20} is lower, and the pore size distribution becomes broader.

[0062]

APPLICATION EXAMPLE 2

In Application Example 2, in the same way as in Application Example 1, aggregate particles were prepared using mullite particles and Scherben particles with various aspect ratios, 50% particle sizes, and particle size distributions. A filtering film was then formed to get filters.

[0063]

[Table 3]

	Aggregate particles										Base material					Filtering film		Filtering layer's maximum pore size			
	Composition		Particle size distribution						Proportion of particles with aspect ratio of 1.1 or smaller in the feed material	Average pore size				Flexural strength	Water permeability	50% particle size of aggregate particles					
			Type of aggregate 1	Type of aggregate 2	D50 x 0.7	D20	D50	D80		D50 x 1.3	%	d50 x 0.75	d20			d50	d80		d50 x 1.25	Intermediate layer	Filtering layer
	μm	μm							μm					μm	μm						
Comparative Example 2-1	M2	20	M1	80	52	63	74	86	96	80	%	12.3	13.8	16.4	19.1	20.5	19.3	71.5	-	-	-
Application Example 2-1	M2	25	M1	75	52	60	74	86	96	75	%	12.0	12.9	16.0	19.1	20.0	34.3	71.5	3.6	0.7	<1.8
Application Example 2-2	M2	50	M1	50	51	54	73	87	95	50	%	11.7	11.9	15.7	18.6	19.6	34.8	70.3	3.6	0.7	<1.8
Application Example 2-3	M2	75	M1	25	49	52	70	88	91	25	%	11.0	11.3	14.7	18.0	18.3	36.6	66.8	3.6	0.7	<1.8
Comparative Example 2-2	M2	80	M1	20	48	47	68	88	88	20	%	10.6	9.3	14.1	18.3	17.6	37.8	64.5	3.6	0.7	3.3
Comparative Example 2-3	M3	20	M1	80	53	65	76	87	99	80	%	12.1	13.6	16.1	18.2	20.1	18.1	73.8	-	-	-
Application Example 2-4	M3	25	M1	75	53	65	76	88	99	75	%	12.5	14.2	16.7	19.6	20.8	33.1	73.8	3.6	0.7	<1.8
Application Example 2-5	M3	50	M1	50	54	64	77	92	100	50	%	12.7	13.9	17.0	20.2	21.2	32.5	75.0	3.6	0.7	<1.8
Application Example 2-6	M3	75	M1	25	54	63	77	97	100	25	%	12.9	13.8	17.2	21.3	21.5	32.5	75.0	3.6	0.7	<1.8
Comparative Example 2-4	M3	80	M1	20	55	63	78	101	101	20	%	13.1	13.7	17.5	22.8	21.9	31.9	76.2	3.6	0.7	5.3
Comparative Example 2-5	S1	20	M1	80	52	64	74	87	96	80	%	12.4	14.1	16.5	19.2	20.6	19.3	71.5	-	-	-
Application Example 2-7	S1	25	M1	75	52	63	74	87	96	75	%	12.0	13.5	16.0	19.1	20.0	34.3	71.5	3.6	0.7	<1.8
Application Example 2-8	S1	50	M1	50	51	61	73	87	95	50	%	11.7	12.9	15.7	18.6	19.6	34.8	70.3	3.6	0.7	<1.8
Application Example 2-9	S1	75	M1	25	50	57	71	88	92	25	%	11.6	12.1	15.4	18.7	19.3	36.0	68.0	3.6	0.7	<1.8
Comparative Example 2-6	S1	80	M1	20	49	56	70	88	91	20	%	11.4	11.8	15.2	19.2	19.0	36.6	66.8	3.6	0.7	4.8

[0064]

(RESULTS)

As can be seen in Table 3, in Application Examples 2-1 to 2-9, in which the proportion of the spherical particles among the aggregate particles and the 50% particle size are controlled to within the ranges defined in this invention, good results were obtained with respect to the base material's flexural strength, base material's water permeability, and the maximum pore size of the filtering layer.

[0065]

On the other hand, in Comparative Examples 2-1, 2-3, and 2-5, in which the proportion of the spherical particles among the aggregate particles is 80 wt% or more, the base material's flexural strength is much lower (20 MPa or lower). In Comparative Examples 2-2, 2-4, and 2-6, in which the proportion of the spherical particles among the aggregate particles is less than 20 wt%, the maximum pore size of the filtering layer is too large. The fine structure inside the base material becomes non-uniform, and when the film is formed, slurry unevenly attaches to the base material.

[0066]

EFFECTS OF THE INVENTION

For the base material for a honeycomb filter of this invention, the 50% particle size and the mass proportion of the spherical particles among the aggregate particles are controlled to within prescribed ranges, respectively. Consequently, the mechanical strength is high and the fluid permeability is also high. Also, when the particle size distribution of the aggregate particles is controlled to within a prescribed range, the pore size distribution of the base material is sharp.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic diagram illustrating the general constitution of a honeycomb filter. It is an overall oblique view of the filter.

Figure 2 is a schematic diagram illustrating an example of the film-forming equipment used in the filtering film-forming method.

BRIEF DESCRIPTION OF PART NUMBERS

- 1 Porous base material
- 2, 3 Flanges
- 4 O-ring
- 5 Bolt
- 6 Vacuum chamber
- 7 Slurry pump
- 8 Storing container
- 9 Film forming slurry
- 10 Pipeline
- 11, 14 Valves
- 12 Inner wall of through holes of porous base material
- 13 Vacuum pump
- 15, 16 Pressure gauges
- 17 Through hole
- A Inlet port
- B Outlet port
- 21 Filter
- 22 Base material
- 23 Cell

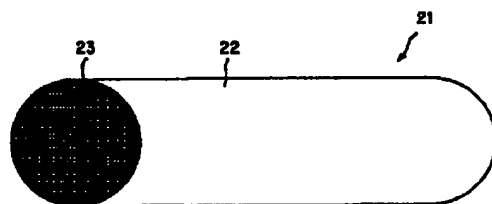


Figure 1

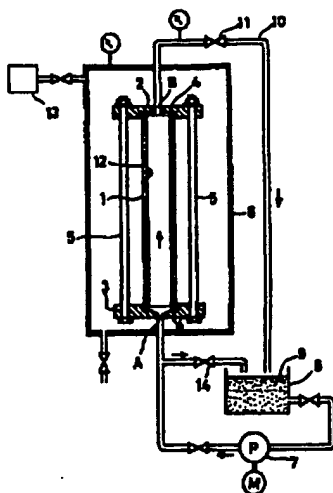


Figure 2

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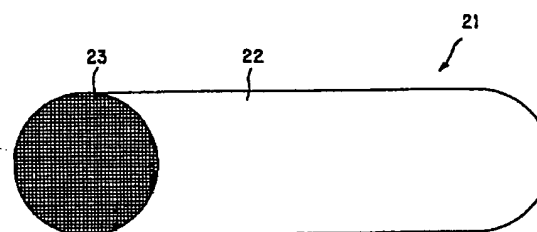
GA11 GA14 GA21 HA04 HA15

(54) 【発明の名称】 ハニカムフィルタ用基材及びその製造方法

(57) 【要約】

【課題】 機械的強度が高く、流体透過量が大きいハニカムフィルタ用基材を提供する。

【解決手段】 多数のセル23を有するハニカム構造の多孔体からなるハニカムフィルタ用の基材22である。基材22を構成する骨材粒子の50%粒子径 (D_{50}) を $40 \sim 100 \mu m$ の範囲内とし、かつ、骨材粒子の20質量%超、80質量%未満はアスペクト比1.1以下の球状粒子、残部はアスペクト比が球状粒子の1.2倍以上の非球状粒子から構成する。



【特許請求の範囲】

【請求項1】 多数のセルを有するハニカム構造の多孔体からなるハニカムフィルタ用の基材であって、当該基材を構成する骨材粒子の50%粒子径 (D_{50}) が40~100 μm の範囲内にあり、かつ、当該骨材粒子の20質量%超、80質量%未満はアスペクト比1.1以下の球状粒子、残部はアスペクト比が前記球状粒子の1.2倍以上の非球状粒子からなることを特徴とするハニカムフィルタ用基材。

【請求項2】 骨材粒子の粒度分布が下記式(1)及び下記式(2)の関係を満たす請求項1に記載のハニカムフィルタ用基材。

$$0.7 \times D_{50} \leq D_{20} \quad \cdots (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad \cdots (2)$$

(但し、 D_{20} : 20%粒子径、 D_{50} : 50%粒子径、 D_{80} : 80%粒子径)

【請求項3】 多数のセルを有するハニカム構造の多孔体からなるハニカムフィルタ用の基材であって、50%細孔径 (d_{50}) が5~25 μm の範囲内にあり、かつ、水銀圧入法により測定した細孔径分布が下記式(3)及び下記式(4)の関係を満たすハニカムフィルタ用基材。

$$0.75 \times d_{50} \leq d_{20} \quad \cdots (3)$$

$$d_{80} \leq 1.25 \times d_{50} \quad \cdots (4)$$

(但し、 d_{20} : 20%細孔径、 d_{50} : 50%細孔径、 d_{80} : 80%細孔径)

【請求項4】 骨材粒子を含む坯土を、ハニカム構造と相補的な形状を有する押出用口金から押し出すことにより成形する工程を含むハニカムフィルタ用基材の製造方法であって、

50%粒子径 (D_{50}) が40~100 μm の範囲内にあり、かつ、アスペクト比が1.1以下である球状粒子の比率が20質量%超、80質量%未満、残部はアスペクト比が前記球状粒子の1.2倍以上である非球状粒子からなる骨材粒子から調製した坯土を使用することを特徴とするハニカムフィルタ用基材の製造方法。

【請求項5】 球状粒子を噴霧乾燥法により得る請求項4に記載のハニカムフィルタ用基材の製造方法。

【請求項6】 坯土を調製する骨材粒子の粒度分布が、下記式(1)及び下記式(2)の関係を満たす請求項4又は5に記載のハニカムフィルタ用基材の製造方法。

$$0.7 \times D_{50} \leq D_{20} \quad \cdots (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad \cdots (2)$$

(但し、 D_{20} : 20%粒子径、 D_{50} : 50%粒子径、 D_{80} : 80%粒子径)

【請求項7】 請求項1~3のいずれか一項に記載のハニカムフィルタ用基材のセル内周面に、セル内周面に比して50%細孔径が小さい濾過膜を少なくとも1層備えたハニカムフィルタ。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は多数のセルを有するハニカム構造の多孔体からなるハニカムフィルタ用基材に関し、詳しくは機械的強度が高く、流体透過量が大きいハニカムフィルタ用基材に関する。

【0002】

【従来の技術】 ハニカムフィルタは、例えば図1に示すような多数のセル23を有するハニカム構造の多孔体を基材22とするフィルタであり、多数のセル23に供給されたガス、液体等の被処理流体が多孔体の細孔を透過する際に濾過が行われるため、単位体積あたりの濾過面積が大きい集塵フィルタ、固液分離フィルタとして利用されている。

【0003】 例えば、フィルタ21をハウジング内に收容し、基材22の外周面側と端面側とをオーリング等で気密的に隔離する構造とすると、セル23内に供給された被処理流体のうち基材の細孔内を透過した濾過流体のみを外周面側から流出させ、濾過されなかった被処理流体を端面側から回収するクロスフローフィルタとして利用することができる。

【0004】 ハニカムフィルタにおいては、セル23の内周面に、基材の細孔に比して更に細孔径が小さい濾過膜(0.01~1.0 μm 程度)を少なくとも1層備える構造とし、基材内部の細孔径を極力大きく構成することが理想的である。このような構造では、細孔径が小さい濾過膜により濾過性能を確保する一方、細孔径が大きく(1~数100 μm 程度)、内部の流動抵抗が低い基材により流体透過量を増加させることが期待できるからである。

【0005】 一般に、ハニカムフィルタ用の基材は、骨材粒子を含む坯土を、ハニカム構造と相補的な形状を有する押出用口金から押し出すことにより成形する方法により製造される。従来、細孔径が大きい基材を得る方法としては、①骨材粒子の粒径を大きくすることにより骨材粒子間の間隙部である細孔を大きくする方法(以下「第1の方法」という。)、或いは②基材焼成時に焼失する有機物(ピッチ、コークス等)を坯土中に添加することにより、空隙部を形成させ通常と比較して細孔を大きくする方法(以下「第2の方法」という。)、等が採用されてきた。

【0006】

【発明が解決しようとする課題】 しかしながら、第1の方法では、得られた基材が、フィルタとしての使用に耐え得る機械的強度を備えていないという問題があった。具体的には、基材のセル内周面に濾過膜を製膜する工程におけるハンドリングで破損するため製品歩留まりが低下したり、或いはフィルタとして使用する際に逆洗浄の圧力で破損する等の不具合があった。

【0007】 また、第2の方法は、細孔径が大きくなり難く透水量が増加し難いことに加えて、基材焼成時に

有機物が急激に燃焼するため、熱衝撃により基材にクラックを生じるという問題があった。

【0008】 即ち、従前においては、機械的強度が高く、流体透過量が大きいハニカムフィルタ用の基材は存在しておらず、そのような基材が切望されている。本発明は、このような従来技術の問題点に鑑みてなされたものであって、その目的とするところは、機械的強度が高く、流体透過量が大きいハニカムフィルタ用基材を提供することにある。

【0009】

【課題を解決するための手段】 本発明者らが鋭意検討した結果、基材を構成する骨材粒子の50%粒子径及び球状粒子の質量比を所定の範囲内に制御することにより、従来技術の問題点を解決できることに想到して本発明を完成した。

【0010】 即ち、本発明によれば、多数のセルを有するハニカム構造の多孔体からなるハニカムフィルタ用の基材であって、当該基材を構成する骨材粒子の50%粒子径 (D_{50}) が40~100 μm の範囲内にあり、かつ、当該骨材粒子の20質量%超、80質量%未満はアスペクト比1.1以下の球状粒子、残部はアスペクト比が前記球状粒子の1.2倍以上の非球状粒子からなることを特徴とするハニカムフィルタ用基材が提供される。

【0011】 上記ハニカムフィルタ用基材は、骨材粒子の粒度分布が下記式(1)及び下記式(2)の関係を満たすことが好ましい。

$$0.7 \times D_{50} \leq D_{20} \quad \cdots (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad \cdots (2)$$

(但し、 D_{20} : 20%粒子径、 D_{50} : 50%粒子径、 D_{80} : 80%粒子径)

【0012】 また、本発明によれば、多数のセルを有するハニカム構造の多孔体からなるハニカムフィルタ用の基材であって、50%細孔径 (d_{50}) が5~25 μm の範囲内にあり、かつ、水銀圧入法により測定した細孔径分布が下記式(3)及び下記式(4)の関係を満たすハニカムフィルタ用基材が提供される。

$$0.75 \times d_{50} \leq d_{20} \quad \cdots (3)$$

$$d_{80} \leq 1.25 \times d_{50} \quad \cdots (4)$$

(但し、 d_{20} : 20%細孔径、 d_{50} : 50%細孔径、 d_{80} : 80%細孔径)

【0013】 更に、本発明によれば、骨材粒子を含む坏土を、ハニカム構造と相補的な形状を有する押出用口金から押し出すことにより成形する工程を含むハニカムフィルタ用基材の製造方法であって、50%粒子径 (D_{50}) が40~100 μm の範囲内にあり、かつ、アスペクト比が1.1以下である球状粒子の比率が20質量%超、80質量%未満、残部はアスペクト比が前記球状粒子の1.2倍以上である非球状粒子からなる骨材粒子から調製した坏土を使用することを特徴とするハニカムフィルタ用基材の製造方法が提供される。

【0014】 本発明の製造方法においては、球状粒子を噴霧乾燥法により得ることが好ましく、坏土を調製する骨材粒子の粒度分布が、下記式(1)及び下記式(2)の関係を満たすことが好ましい。

$$0.7 \times D_{50} \leq D_{20} \quad \cdots (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad \cdots (2)$$

(但し、 D_{20} : 20%粒子径、 D_{50} : 50%粒子径、 D_{80} : 80%粒子径)

【0015】 更にまた、本発明によれば、上記のハニカムフィルタ用基材のセル内周面に、セル内周面に比して50%細孔径が小さい濾過膜を少なくとも1層備えたハニカムフィルタが提供される。

【0016】

【発明の実施の形態】 本発明のハニカムフィルタ用基材は、基材を構成する骨材粒子の50%粒子径及び球状粒子の質量比を所定の範囲内に制御したものである。本発明のハニカムフィルタ用基材は、機械的強度が高く、流体透過量が大きい。以下、本発明について詳細に説明する。

【0017】 (1) 基材

本発明のハニカムフィルタ用基材(以下、単に「基材」という。)は、骨材粒子のうち少なくとも1種をアスペクト比が1.1以下である球状粒子としたものである。このような球状粒子を骨材粒子とすることにより、基材焼成後においても骨材粒子間に確実に間隙部(即ち細孔)が形成され、流体の透過量を大きくすることができる。具体的には、前記球状粒子を骨材粒子中に20質量%以上含むことにより流体透過量を増加させ、基材内部の微構造を均一化する効果を得ることができる。

【0018】 但し、基材を構成する骨材粒子の全てを上記球状粒子とすると骨材粒子間の結合が弱くなり、基材の機械的強度が低下する。従って、前記球状粒子は骨材粒子の20質量%以上とすることに加え、その上限を80質量%とする必要がある。

【0019】 骨材粒子のうち球状粒子以外の残部についてはアスペクト比が前記球状粒子の1.2倍以上である非球状粒子により構成する。即ち、球状粒子としてアスペクト比1.0の粒子を用いた場合には1.2以上、1.1のものをを用いた場合であれば1.32以上のアスペクト比を有する粒子が非球状粒子となる。非球状粒子は流体透過量を増加させるという観点からは好ましくないが、骨材粒子間の結合を強化する効果を有し、基材の機械的強度を向上させる作用がある。

【0020】 なお、本発明にいう「アスペクト比」とは、粉末状態においては走査型電子顕微鏡で撮影した写真から任意に選択した20個の骨材粒子のアスペクト比(長辺と短辺の比)の平均値、焼結体においては、焼結体の切断面に樹脂(例えばエポキシ樹脂)を塗布して穴埋めし、更に鏡面仕上げを行った面について同様に算出したアスペクト比の平均値である。

【0021】 球状粒子、非球状粒子は、既述のアスペクト比を満たしていることに加え、50%粒子径

(D_{50}) が所定の範囲、具体的には40~100 μm の範囲内に制御されていることが必要である。50%粒子径(D_{50})が40 μm 未満の場合には流体透過量が減少する点において、100 μm 超となる場合には基材の機械的強度が低下する点においていずれも好ましくない。また、50%粒子径(D_{50})を40~100 μm の範囲内とすることにより、基材の50%細孔径(d_{50})も5~25 μm (水銀圧入法)の範囲内に制御される。

【0022】 なお、本発明に言う「x%粒子径」とは、粉末状態においては篩分け法により測定した粒子径である。具体的には、公称目開き径の異なる複数の篩を、上段ほど目開き径が大きくなるように多段に積重したものを用意し、最上段の篩に粒子径の測定対象である粉体試料を注入し、振とう機で15分間振とうした後、各段の篩上にある粉末質量とその篩の目開き径との関係から粒度分布曲線を作成し、積算質量がx%となる粒子径をx%粒子径と規定した。

【0023】 球状粒子、非球状粒子は、既述の球状粒子比率、50%粒子径(D_{50})を満たしていることに加え、粒度分布が所定の範囲に制御されていること、具体的には下記式(1)及び下記式(2)の関係を満たすことが好ましい。

$$0.7 \times D_{50} \leq D_{20} \quad \cdots (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad \cdots (2)$$

(但し、 D_{20} : 20%粒子径、 D_{50} : 50%粒子径、 D_{80} : 80%粒子径)

【0024】 骨材粒子の粒度分布が上記式(1)及び上記式(2)の関係を満たす基材は細孔径分布がシャープとなるからである。具体的には、水銀圧入法により測定した細孔径分布が下記式(3)及び下記式(4)の関係を満たす範囲内に制御された基材となる。

$$0.75 \times d_{50} \leq d_{20} \quad \cdots (3)$$

$$d_{80} \leq 1.25 \times d_{50} \quad \cdots (4)$$

(但し、 d_{20} : 20%細孔径、 d_{50} : 50%細孔径、 d_{80} : 80%細孔径)

【0025】 一方、上記式(1)を満たさない場合には微粒成分が多くなることに起因して基材の骨材粒子間の空隙部が閉塞され、流体透過量が減少するおそれがある。また、上記式(2)を満たさない場合には、骨材粒子間の空隙部が大きくなるが、製膜工程において製膜用スラリーが当該空隙部に入り込み閉塞するため、やはりフィルタの流体透過量は低下するおそれがある。

【0026】 なお、本発明にいう「x%細孔径」とは、下記式(5)を原理式とする水銀圧入法により測定した細孔径である。具体的には、乾燥した基材に対して徐々に圧力を上昇させながら水銀を圧入すると、径の大きい細孔から順に水銀が圧入されて水銀の累積容量が増加していき、最終的に全ての細孔が水銀で満たされる

と、累積容量は衡量に達する。本発明においては、累積容量がx%となった際の圧力Pから算出された細孔径dをx%細孔径と規定した。

$$d = -\gamma \times \cos \theta / P \quad \cdots (5)$$

(但し、d: 細孔径、 γ : 表面張力、 θ : 接触角、P: 圧力)

【0027】 (2) 製造方法

ハニカムフィルタ用の基材は、骨材粒子を含む坯土を、ハニカム構造と相補的な形状を有する押出用口金から押し出すことにより成形し、当該成形体を乾燥し、焼成することにより得られる。本発明の基材を製造するためには、坯土を調製する際にアスペクト比、50%粒子径、粒度分布を既述の範囲内に制御した骨材粒子を使用すればよい。

【0028】 即ち、50%粒子径(D_{50})が40~100 μm の範囲内にあり、かつ、アスペクト比が1.1以下である球状粒子の比率が20質量%超、80質量%未満、残部はアスペクト比が前記球状粒子の1.2倍以上である非球状粒子からなる骨材粒子から坯土を調製する。基材の細孔径分布をシャープにしたい場合には、当該骨材粒子の粒度分布が下記式(1)及び下記式(2)の関係を満たすようにする。

$$0.7 \times D_{50} \leq D_{20} \quad \cdots (1)$$

$$D_{80} \leq 1.3 \times D_{50} \quad \cdots (2)$$

(但し、 D_{20} : 20%粒子径、 D_{50} : 50%粒子径、 D_{80} : 80%粒子径)

【0029】 調製の方法としては、例えば市販のセラミック原料をそのまま、或いはこれを粉碎・分級したものを骨材粒子とし、2種以上の骨材粒子を既述の条件を満たすように適宜混合する方法などが挙げられる。

【0030】 本発明の製造方法においては、球状粒子を噴霧乾燥法により得ることが好ましい。球状粒子は粉碎機や混合機(ボールミル等)で粉碎・混合する方法により調製したものを使用しても良いが、液状とした原料をスプレードライヤーにより造粒・乾燥し、焼成する噴霧乾燥法によれば、比較的容易にアスペクト比1.1以下の球状粒子が得られるからである。また、噴霧乾燥法により得られた粒子は粉碎により得られた粒子と比較して表面が平滑であるため、押出成形用口金を痛めずその耐用期間が10倍程度に長くなる点においても好ましい。

【0031】 本発明の製造方法は、坯土を調製する際にアスペクト比、50%粒子径、所望により粒度分布を既述の範囲内に制御した骨材粒子を使用することを除き、従来公知の製造方法と同様の方法により製造することが可能である。

【0032】 坯土は、骨材粒子の他、分散媒、有機バインダ、必要により無機結合材、界面活性剤、可塑剤等を添加し、混練し成形原料とする。

【0033】 骨材粒子としては、アルミナ、ムライ

ト、セルベン、コーゼライト、炭化珪素或いはこれらの混合物等を、分散媒としては、水等を、有機バインダとしてはメチルセルローズ等を用いることができる。

【0034】 無機結合材は、骨材粒子の結合を強化するための添加材であり、粒径1 μ m未満のアルミナ、シリカ、ジルコニア、チタニア、ガラスフリット、長石、コーゼライトのうちの1種又は2種以上の混合物を使用することができる。なお、無機結合材はセラミック粒子ではあるが本発明にいう骨材粒子には包含されない。

【0035】 無機結合材は、骨材粒子の質量を100質量%とした場合において、これに対し、15質量%以上、35質量%以下に相当する量を添加することが好ましい。15質量%未満であると基材の強度が低下する一方、35質量%超となると十分な強度は得られるものの骨材粒子の間に無機結合材が止まるため、基材内部の細孔を閉塞し流体透過量を低下させるおそれがあるからである。

【0036】 坯土を所望の形状に押出成形し、乾燥・焼成することによりハニカム構造の基材を製造することができる。例えば、単軸、2軸、或いは多軸のスクリー押出機やプランジャー押出機等の従来公知の押出機に投入した坯土を、基材のハニカム構造と相補的な形状を有する押出用口金から押し出すことにより成形体を得ることができる。

【0037】 口金の形状により、基材の端面形状（円形、正方形、長方形、六角形等）、端面外径（円形の場合30～200mm ϕ ）、セルの形状（円形、四角形、六角形等）、セルの内接孔直径（通常は2～5mm ϕ 程度）等を所望の形状とすることが可能である。基材のサイズは特に限定されないが、長手方向の全長が150～2000mm程度のものが汎用される。

【0038】 (3) フィルタ

上述の基材のセル内周面に、骨材粒子を含む製膜用スラリーを付着せしめた後、当該製膜体を乾燥・焼成する方法により濾過膜を形成することができ、ハニカムフィルタを得ることができる。

【0039】 例えば、骨材粒子を水等の分散媒中に分散し、必要に応じ有機バインダ、pH調整剤、界面活性剤等を添加することにより製膜用のスラリーとし、従来公知の方法、例えばディップ製膜法、本出願人が既に開示した特公昭63-66566号公報に記載の濾過製膜法等を用いてセル内周面に成膜して乾燥し、更に当該製膜体を1300℃程度の高温で焼成する等の方法によりフィルタを得ることができる。骨材粒子、分散媒、有機バインダについては基材と同様のものを使用することができる。但し、濾過膜の細孔径を小さくするため骨材粒子の50%粒子径は基材よりも小さくすることが一般的である。

【0040】 また、製膜用スラリーには基材と同様の目的で無機結合材を含有させても良い。濾過膜の場合には、粒径1 μ m未満の粘土、カオリン、チタニアゾル、シリカゾル、ガラスフリット等を用いることができ、骨材粒子及び無機結合材の全質量中に、5質量%以上、25質量%以下の比率で含まれていることが好ましい。

【0041】 なお、濾過膜は少なくとも1層形成することが必要があるが、2層以上形成して複層としてもよい。

【0042】

【実施例】 以下、本発明のフィルタを実施例により更に詳細に説明するが、本発明は下記の実施例により限定されるものではない。

【0043】 基材の骨材粒子となるセラミック原料としては、表1に記載の組成及びアスペクト比を有するアルミナ（A1～A6）、ムライト（M1～M3）、セルベン（S1）を使用した。これらの原料を表2～3に記載の比率で混合して骨材粒子を調製した。

【0044】 なお、A3、M1については、原料を液状とした後スプレードライヤーにより造粒・乾燥し、焼成することによりアスペクト比を1.1以下とした。

【0045】

【表1】

記号	種類	粒度分布					アスペクト比	
		D50 \times 0.7 μ m	D20 μ m	D50 μ m	D80 μ m	D50 \times 1.3 μ m	平均	1.1以下粒子 %
A1	アルミナ	60	62	85	106	111	1.8	0
A2		49	55	70	86	91	1.9	0
A3		53	65	75	85	98	1.1	100
A4		74	92	105	135	137	1.8	0
A5		18	18	26	33	34	1.8	0
A6		53	41	75	105	98	1.7	0
M1	ムライト	53	65	78	85	99	1	100
M2		46	45	65	87	85	1.5	0
M3		55	62	78	104	101	1.8	0
S1	セルベン	49	54	70	87	91	1.8	0

【0046】 (基材)上記骨材粒子に、無機結合材（長石、ガラスフリット等）、水の他、有機バインダとしてメチルセルローズを加えて混練した坯土を押出成形し、外径 ϕ 30mm、直径 ϕ 2.4mmのセルを37本有す

るハニカム構造の押出成形体を得た。無機結合材は骨材粒子の質量を100質量%とした場合において、これに対し25質量%に相当する量を添加した。当該押出成形体を電気炉で1500℃で焼成することにより基材を得た。

【0047】 上記基材は、基材の50%細孔径及び細孔径分布、機械的強度について評価した。

【0048】 基材の50%細孔径及び細孔径分布については、水銀圧入法に従って以下の方法により測定した。まず、基材を端面から25mmの長さだけ切り出し、更にセル4～5個残るように切削して測定用サンプルとし、当該サンプルを水銀中に浸漬した状態で水銀を圧入し、その累積容量を測定することにより20%細孔径、50%細孔径、80%細孔径を算出した。

【0049】 基材の機械的強度については、各成形用坏土を直径φ20mm×長さ100mmの円筒状に押出した成形体を、基材と同様の条件で乾燥し、焼成してなる焼結体を支点間距離80mmとして3点曲げ強度の試験を行うことにより評価した。

【0050】 上記基材は濾過膜を形成してフィルタとしての性能についても評価した。濾過膜は複層構造とし、中間層と濾過層を設けた。

【0051】 中間層及び濾過層の製膜は、特開昭61-238315号公報に記載の濾過成膜法により行った。具体的には、図2に示す真空チャンバ6、貯蔵槽8、ポンプ7、フランジ2、3、配管10等からなる装置に対し、細孔内を水などの液体で置換した基材1のセル内周面側と基材1外周面側とをフランジ2、3、ボルト5で気密的に隔離した状態で固定し、次いで貯蔵槽8内のスラリー9をポンプ7により基材1のセル内に連続的に送液してセル内周面12に接触させながら、真空チャンバ6内を真空ポンプ13により真空排気し、基材1外周面側を減圧状態とする。このような操作により、基材1外周面側とセル内周面12側との間に濾過差圧が付与されるため、基材1のセル内周面12にはスラリーが製膜され、スラリー中の水分は濾液として基材1外周面

側から排出される。

【0052】 (中間層) 基材と同材質で50%粒子径(D_{50})が3.2μmの骨材粒子、無機結合材(長石、ガラスフリット等)、水を27:3:70の質量比で混合してスラリーを調製した。各セルの内周面にスラリーを製膜した後、乾燥し、焼成することにより基材に固着させ中間膜を形成した。

【0053】 (濾過層) 基材と同材質で50%粒子径(D_{50})が0.4μmの骨材粒子、無機結合材(ガラスフリット)、水を9:1:90の質量比で混合してスラリーを調製した。各セルの中間層の表面にスラリーを製膜した後、乾燥し、焼成することにより中間層に固着させ濾過層を形成した。

【0054】 上記のように製造されたフィルタについては、流体透過量を透水量により、濾過性能を濾過層の最大細孔径により評価した。透水量は、水中、6.7kPa以下の減圧下で2時間、フィルタ内の気泡を脱気した後、差圧4.8～9.8kPa、温度25℃の条件で純水をフィルタのセルに注入し、セル内からフィルタ外周面側へ、透過させることにより濾過し、濾過面積当たりの時間当たりの透水量を測定することにより評価した。

【0055】 濾過層の最大細孔径については以下の方法で測定した。ASTM F316に記載のエアフロー法に準拠し、水温20℃の水で湿潤したフィルタに対し、圧力を徐々に上昇させながら加圧エアをセル内周面から送り込み、基材外周面から最初に気泡が確認された圧力Pから算出された細孔径Dを濾過層の最大細孔径とした。

【0056】 (実施例1) 実施例1として、種々の球状粒子比率、50%粒子径、粒度分布を有するアルミナ粒子を骨材粒子として基材を作製し、更に濾過膜を形成してフィルタとした例を示す。

【0057】

【表2】

細孔径が d_{20} が d_{50} の0.75倍以上、 d_{80} が d_{50} の1.25倍以下となっており、細孔径分布がシャープであった。一方、球状粒子比率と50%粒子径を満たしている場合でも、粒度分布が本発明の範囲にない比較例1-10、1-11は基材の細孔径分布において d_{20} が低下し、細孔径分布はブロードとなった。

【0062】（実施例2）実施例2は、実施例1と同様にして、種々のアスペクト比、50%粒子径、粒度分布を有するムライト粒子、セルペン粒子を骨材粒子として基材を作製し、更に濾過膜を形成してフィルタとした例を示す。

【0063】

【表3】

	組成		骨材粒子					基材							濾過層 最大細孔径		
	骨材1 種類	骨材2 種類	粒度分布					アスペクト比			平均細孔径			曲げ強度		透水率	骨材粒子D50 中間層濾過層
			D50×0.7	D20	D50	D80	D50×1.3	1.1以下粒子 原料中比率	d50	d80	d50×1.25						
												%	μm				
比較例2-1	M2	M1	52	63	74	86	96	80	12.3	13.6	16.4	19.1	20.3	19.3	71.5	-	-
実施例2-1	M2	M1	52	60	74	86	86	75	12.0	12.9	16.0	18.1	20.0	34.3	71.5	3.6	0.7
比較例2-2	M2	M0	51	54	73	87	95	50	11.7	11.9	15.7	18.6	18.8	34.8	70.3	3.6	0.7
実施例2-3	M2	M1	49	52	70	88	91	25	11.0	11.3	14.7	18.0	18.3	36.6	68.8	3.6	0.7
比較例2-2	M2	M0	48	47	68	88	88	20	10.8	9.3	14.1	18.3	17.6	37.8	64.5	3.6	0.7
比較例2-3	M3	M0	63	65	76	87	99	80	12.1	13.6	16.1	18.2	20.1	18.1	73.8	-	-
実施例2-4	M3	M1	53	65	76	88	99	75	12.5	14.2	16.7	18.6	20.8	33.1	73.8	3.6	0.7
比較例2-5	M3	M0	54	64	77	92	100	50	12.7	13.9	17.0	20.2	21.2	32.5	75.0	3.6	0.7
実施例2-6	M3	M1	54	63	77	87	100	25	12.8	13.8	17.2	21.3	21.5	32.5	75.0	3.6	0.7
比較例2-4	M3	M0	55	63	78	101	101	20	13.1	13.7	17.5	22.8	21.9	31.9	78.2	3.6	0.7
比較例2-5	S1	M0	52	64	74	87	96	80	12.4	14.1	16.5	18.2	20.6	19.3	71.5	-	-
実施例2-7	S1	M1	52	63	74	87	96	75	12.0	13.5	16.0	18.1	20.0	34.3	71.5	3.6	0.7
比較例2-6	S1	M0	51	61	73	87	95	50	11.7	12.9	15.7	18.6	18.6	34.8	70.3	3.6	0.7
実施例2-8	S1	M1	50	57	71	88	92	25	11.8	12.1	15.4	18.7	19.3	38.0	68.0	3.6	0.7
比較例2-9	S1	M1	49	56	70	88	91	20	11.4	11.8	15.2	19.2	18.0	38.6	66.8	3.6	0.7
比較例2-8	S1	M0	48	56	70	88	91	20	11.4	11.8	15.2	19.2	18.0	38.6	66.8	3.6	0.7

【0064】（結果）表3に示したように、骨材粒子の球状粒子比率、50%粒子径が本発明の範囲内にある実施例2-1～2-9については、基材曲げ強度、基材透水量、濾過層の最大細孔径のいずれも良好な結果を示した。

【0065】一方、骨材粒子中の球状粒子が80質量%以上である比較例2-1、2-3、2-5についてはいずれも基材曲げ強度が20MPa以下と顕著に低下した。骨材粒子中の球状粒子が20質量%以下である比較例2-2、2-4、2-6についてはいずれも濾過層の

最大細孔径が大きくなる傾向があった。基材内部の微構造が不均一であることに起因して、製膜時において、基材へのスラリーの付着が不均一となったためである。

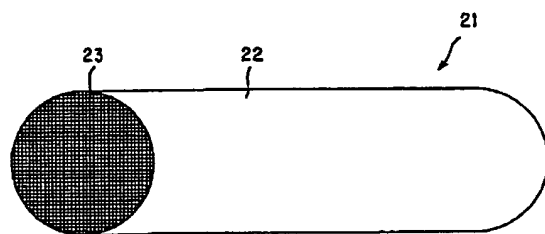
【0066】

【発明の効果】 本発明のハニカムフィルタ用基材は、基材を構成する骨材粒子の50%粒子径及び球状粒子の質量比を所定の範囲内に制御したので、機械的強度が高く、流体透過量が大きい。また、骨材粒子の粒度分布を所定の範囲内に制御した場合には基材の細孔径分布もシャープなものとなる。

【図面の簡単な説明】

【図1】 ハニカムフィルタの一般的な構造を示す概略

【図1】



図であって、フィルタ全体の斜視図である。

【図2】 濾過成膜法に使用する製膜装置の例を示す概略図である。

【符号の説明】

1…多孔質基材、2, 3…フランジ、4…Oリング、5…ボルト、6…真空チャンバ、7…スラリーポンプ、8…貯蔵槽、9…成膜用スラリー、10…配管、11, 14…バルブ、12…多孔質基材の貫通孔内壁、13…真空ポンプ、15, 16…圧力計、17…貫通孔、A…供給口、B…排出口、21…フィルタ、22…基材、23…セル。

【図2】

